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(72) LARSON, BERND, DE  
(72) LIETZMANN, ANDREAS, DE  
(72) LAHN, WOLFGANG, DE  
(72) JUNG, DIETER, DE  
(71) HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN, DE  
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(54) **PROCEDE DE GRANULATION**  
(54) **GRANULATION PROCESS**

(57) The invention relates to a new granulation process in which a surfactant foam obtained by foaming a flowable component containing anionic surfactant acid with a gaseous medium is used as a granulation aid. The surfactant foam preferably has mean pore sizes below 10 mm, preferably below 5 mm and more preferably below 2 mm.





## GRANULATION PROCESS

### Field of the Invention

This invention relates to a process for the production of surfactant granules. More particularly, the invention relates to a process by which it is possible to produce surfactant granules or surfactant-containing components of detergent compositions or complete detergent compositions with or without a reduced number of spray drying steps.

### Background of the Invention

Granular detergent compositions or components for such compositions are largely produced by spray drying. In the spray drying process, the ingredients, such as surfactants, builders etc. containing around 35 to 50% by weight of water, are mixed to form an aqueous suspension, known as a slurry, and the resulting mixture is sprayed into a hot gas stream in spray drying towers, resulting in the formation of the detergent particles. Both the installations for this process and the operation of the process are expensive because most of the water in the slurry has to be evaporated in order to obtain particles having residual water contents of around 5 to 10% by weight. In addition, although the granules produced by spray drying generally show excellent solubility, they have low bulk densities which leads to higher packaging volumes and transportation and storage capacities. The flowability of spray-dried granules is also far from optimal in view of their irregular surface structure which also has an effect on their appearance. Spray drying processes have a number of other disadvantages, so that there has been no shortage of attempts to carry out the production of detergents without any spray drying whatever or at least to have low levels of spray-dried products in the end product.

Thus, *W. Hermann de Groot, I. Adami, G.F. Moretti in "The Manufacture of Modern Detergent Powders", Hermann de Groot Academic Publisher, Wassenaar, 1995, pages 102 et seq.* describe various mixing and granulation processes for the production of detergents. One

feature common to all these processes is that premixed solids are granulated in the presence of the liquid ingredients and optionally dried in a following step.

5 A broad prior art on the non-tower production of detergents also exists in the patent literature. Many of these processes start out from the acid form of anionic surfactants because, in quantitative terms, this class of surfactants represents the largest percentage of deterative substances and because, in the course of their production, anionic surfactants accumulate in the form of the free acids which have to be neutralized to the  
10 corresponding salts.

A new way of producing surfactant granules which avoids the disadvantages of known processes is foam granulation which is described in earlier German patent applications DE 198 44 523.7, DE 198 44 522.9 and DE 198 55 380.3 (all Henkel KGaA).

15 DE 198 44 523.7 discloses a process for the production of surfactant granules in which an anionic surfactant in its acid form and a highly concentrated, aqueous alkaline component are separately exposed to the action of a gaseous medium and then combined and neutralized and both the anionic surfactant in its acid form and the highly concentrated, aqueous  
20 alkaline component are foamed by the gaseous medium and the acidic and alkaline foams formed are combined to form a neutralize foam which is then introduced into a bed of solids in a mixer. According to the teaching of this document, two foams (an acidic foam and an alkaline foam) are combined and the neutralize foam is used as a granulation aid for solids.

25 Earlier German patent application DE 198 44 522.9 discloses a foam granulation process in which the foam serving as a granulation aid is not formed by combining an acidic foam and an alkaline foam. Instead, the document in question discloses a process for the production of surfactant granules in which a surfactant-containing flowable component is exposed  
30 to the action of a gaseous medium, the surfactant-containing flowable

component being foamed by the gaseous medium and the surfactant-containing foam formed subsequently being added to a bed of solids in a mixer. According to the disclosure of the document in question, nonionic surfactants or salts of anionic surfactant acids, for example, may be used  
5 as the surfactant-containing flowable components. There is no mention in this document of the use of the anionic surfactant acids in the form of a foam.

Foam granulation processes with foamed anionic surfactant acid are disclosed in earlier German patent application DE 198 55 380.3. This  
10 document relates to a process for the production of surfactant granules in which an anionic surfactant in its acid form is neutralized and granulated with a solid neutralizing agent, the solid neutralizing agent being added to the anionic surfactant in its acid form and being foamed to form a neutralizate foam which is subsequently added to a bed of solids in a  
15 mixer. The neutrally reacting foam serving as granulation aid is formed from the anionic surfactant acid and the solid neutralizing agent. A process in which an acidic surfactant-containing foam serves as granulation aid is not described in this document either.

Now, the problem addressed by the present invention was to further  
20 develop the field of foam granulation and to provide a process which would enable surfactant granules for detergents to be produced with or without a reduced input of spray drying steps and which would start out directly from the acid form of the anionic surfactants. In addition, the need to dry the granules formed would preferably be eliminated altogether.

## 25 **Description of the Invention**

The present invention relates to a process for the production of surfactant granules in which a surfactant-containing flowable component is exposed to the action of a gaseous medium and foamed and the surfactant-containing foam formed is subsequently added to a bed of solids

initially introduced into a mixer, characterized in that the surfactant-containing flowable component contains anionic surfactant acid(s).

In contrast to the prior art cited in the foregoing, an acidic foam, i.e. a foam with a pH value below 7, is used as granulation aid in the process according to the invention. In preferred variants of the process according to the invention, the bed of solids to be granulated contains alkaline ingredients so that a neutralization reaction takes place during the granulation step. The process according to the invention has the advantage over the well-known addition of anionic surfactant acids in liquid form that the acid is carefully introduced into the mixer and is very uniformly distributed. The formation of large lumps or the formation of acid clusters, which could lead to discoloration of the granules and to unwanted reactions with sensitive ingredients (for example perfume) of the final detergent, are thus effectively avoided.

The term "foam" used in the present specification characterizes structures of gas-filled, spherical or polyhedral cells (pores) which are defined by liquid, semiliquid or highly viscous cell walls.

If the concentration by volume of the gas forming the foam is less than 74% for homodisperse distribution, the gas bubbles are spherical on account of the surface-reducing effect of the interfacial tension. Beyond the close packing limit, the bubbles are deformed to polyhedral lamellae which are defined by ca. 4-600 nm thin skins. The cell walls - joined via by so-called nodal points - form a coherent structure. The foam lamellae extend between the cell walls (closed-cell foam). If the foam lamellae are destroyed or if they flow back into the cell walls at the end of foaming, an open-cell foam is obtained. Foams are thermodynamically unstable because surface energy can be obtained by making the surface smaller. Accordingly, the stability and hence the existence of the foams according to the invention depends on the extent to which it is possible to prevent their self-destruction.

To produce the foam, the gaseous medium is injected into the flowable component containing anionic surfactant acid. Alternatively, foaming can be achieved by intensive beating, shaking, spraying or stirring of the liquid in the particular gas atmosphere. Because it provides for easier foaming and can be better controlled and carried out, foam generation by injection of the gaseous medium ("mechanical blowing") is distinctly preferred to the other variants for the purposes of the present invention. Depending on the required process variant, mechanical blowing takes place continuously or discontinuously via perforated plates, sintered disks, sieve insets, Venturi nozzles, inline mixers, homogenizers or other standard systems.

Any gases or gas mixtures may be used as the gaseous medium for foaming. Examples of gases used in the art are nitrogen, oxygen, noble gases and noble gas mixtures, carbon dioxide, etc. For reasons of cost, the process according to the invention is preferably carried out with air as the gaseous medium.

The process according to the invention comprises the independent steps of producing foam from a flowable component containing an anionic surfactant acid and adding the foam produced to a bed of solids agitated in a mixer where the foam acting as a granulation aid. The ingredients of the surfactant-containing foam produced in the first step are described hereinafter.

The surfactant-containing flowable component contains at least interfacially active substances from the group of anionic surfactants present at least partly in their acid form, i.e. in non-neutralized form. The surfactant-containing flowable component may additionally contain other surface-active compounds from the groups of anionic, nonionic, zwitterionic or cationic surfactants. The surfactant content of the flowable surfactant-containing component may vary within wide limits. According to the invention, preferred processes are characterized in that the surfactant-

containing flowable component contains one or more anionic surfactant acid(s) in quantities of 20 to 100% by weight, preferably 50 to 95% by weight and more preferably 60 to 90% by weight, based on the surfactant-containing component.

5       The process according to the invention comprises the independent steps of producing foam from an anionic surfactant in its acid form on the one hand and adding the foam produced to a bed of solids agitated in a mixer on the other hand. The most important anionic surfactant acids usable in accordance with the invention are described in the following.

10       One or more representatives from the group of carboxylic acids, sulfuric acid semiesters and sulfonic acids, preferably from the group of fatty acids, fatty alkyl sulfuric acids and alkylaryl sulfonic acids, is/are preferably used as the anionic surfactants in acid form. In order to obtain adequate surface-active properties, the compounds mentioned should  
15       have relatively long hydrocarbon chains, i.e. should contain at least 6 carbon atoms in the alkyl or alkenyl group. The C-chain distributions of the anionic surfactants are normally in the range from 6 to 40, preferably in the range from 8 to 30 and more preferably in the range from 12 to 22 carbon atoms.

20       On an industrial scale, carboxylic acids - which are used in the form of their alkali metal salts as soaps in detergents - are largely obtained from native fats and oils by hydrolysis. Whereas alkaline saponification, which was practised as long ago as the last century, led directly to the alkali metal salts (soaps), only water is now industrially used for hydrolysis, splitting the  
25       fats into glycerol and the free fatty acids. Industrially used processes include, for example, hydrolysis in an autoclave and continuous high-pressure hydrolysis. According to the invention, carboxylic acids suitable for use as the anionic surfactants in acid form are, for example, hexanoic acid (caproic acid), heptanoic acid (oenanthic acid), octanoic acid (caprylic acid),  
30       nonanoic acid (pelargonic acid), decanoic acid (capric acid),



undecanoic acid, etc. According to the invention, it is preferred to use fatty acids, such as dodecanoic acid (lauric acid), tetradecanoic acid (myristic acid), hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), eicosanoic acid (arachic acid), docosanoic acid (behenic acid),

5 tetracosanoic acid (lignoceric acid), hexacosanoic acid (cerotic acid), triacontanoic acid (melissic acid) and the unsaturated species 9c-hexadecenoic acid (palmitoleic acid), 6c-octadecenoic acid (petroselic acid), 6t-octadecenoic acid (petroselaidic acid), 9c-octadecenoic acid (oleic acid), 9t-octadecenoic acid (elaidic acid), 9c,12c-octadecadienoic acid

10 (linoleic acid), 9t,12t-octadecadienoic acid (linolaidic acid) and 9c,12c,15c-octadecatrienoic acid (linolenic acid). For reasons of cost, technical mixtures of the individual acids obtainable from the hydrolysis of fats are used in preference to the pure species. Mixtures such as these are, for example,

15 coconut oil fatty acid (ca. 6% by weight C<sub>8</sub>, 6% by weight C<sub>10</sub>, 48% by weight C<sub>12</sub>, 18% by weight C<sub>14</sub>, 10% by weight C<sub>16</sub>, 2% by weight C<sub>18</sub>, 8% by weight C<sub>18'</sub>, 1% by weight C<sub>18''</sub>), palm kernel oil fatty acid (ca. 4% by weight C<sub>8</sub>, 5% by weight C<sub>10</sub>, 50% by weight C<sub>12</sub>, 15% by weight C<sub>14</sub>, 7% by weight C<sub>16</sub>, 2% by weight C<sub>18</sub>, 15% by weight C<sub>18'</sub>, 1% by weight C<sub>18''</sub>), tallow fatty acid (ca. 3% by weight C<sub>14</sub>, 26% by weight C<sub>16</sub>, 2% by weight

20 C<sub>16'</sub>, 2% by weight C<sub>17</sub>, 17% by weight C<sub>18</sub>, 44% by weight C<sub>18'</sub>, 3% by weight C<sub>18''</sub>, 1% by weight C<sub>18'''</sub>), hydrogenated tallow fatty acid (ca. 2% by weight C<sub>14</sub>, 28% by weight C<sub>16</sub>, 2% by weight C<sub>17</sub>, 63% by weight C<sub>18</sub>, 1% by weight C<sub>18'</sub>), technical oleic acid (ca. 1% by weight C<sub>12</sub>, 3% by weight C<sub>14</sub>, 5% by weight C<sub>16</sub>, 6% by weight C<sub>16'</sub>, 1% by weight C<sub>17</sub>, 2% by weight

25 C<sub>18</sub>, 70% by weight C<sub>18'</sub>, 10% by weight C<sub>18''</sub>, 0.5% by weight C<sub>18'''</sub>), technical palmitic/stearic acid (ca. 1% by weight C<sub>12</sub>, 2% by weight C<sub>14</sub>, 45% by weight C<sub>16</sub>, 2% by weight C<sub>17</sub>, 47% by weight C<sub>18</sub>, 1% by weight C<sub>18'</sub>) and soybean oil fatty acid (ca. 2% by weight C<sub>14</sub>, 15% by weight C<sub>16</sub>, 5% by weight C<sub>18</sub>, 25% by weight C<sub>18'</sub>, 45% by weight C<sub>18''</sub>, 7% by weight

30 C<sub>18'''</sub>).

Sulfuric acid semiesters of relatively long-chain alcohols are also anionic surfactants in their acid form and may be used in the process according to the invention. Their alkali metal salts, more especially sodium salts, the fatty alcohol sulfates, can be industrially obtained from fatty alcohols which are reacted with sulfuric acid, chlorosulfonic acid, amidosulfonic acid or sulfur trioxide to form the corresponding alkyl sulfuric acids and then neutralized. The fatty alcohols are obtained from the corresponding fatty acids or fatty acid mixtures by high-pressure hydrogenation of the fatty acid methyl esters. In quantitative terms, the most important industrial process for the production of fatty alkyl sulfuric acids is sulfonation of the alcohols with  $\text{SO}_3$ /air mixtures in special cascade, falling-film or tube-bundle reactors.

Another class of anionic surfactant acids which may be used in the process according to the invention are the alkyl ether sulfuric acids of which the salts, the alkyl ether sulfates, are distinguished from the alkyl sulfates by greater solubility in water and lower sensitivity to water hardness (solubility of the Ca salts). Like the alkyl sulfuric acids, alkyl ether sulfuric acids are synthesized from fatty alcohols which are reacted with ethylene oxide to form the corresponding fatty alcohol ethoxylates. Propylene oxide may be used instead of ethylene oxide. The subsequent sulfonation with gaseous sulfur trioxide in short-time sulfonation reactors gives yields of more than 98% of the corresponding alkyl ether sulfuric acids.

Alkane sulfonic acids and olefin sulfonic acids may also be used as anionic surfactants in acid form for the purposes of the present invention. Alkane sulfonic acids may contain the sulfonic acid group terminally bound (primary alkane sulfonic acids) or along the C-chain (secondary alkane sulfonic acids), only the secondary alkane sulfonic acids being of commercial importance. They are prepared by sulfochlorination or sulfoxidation of linear hydrocarbons. Where sulfochlorination is carried out

by *Reed's* method, n-paraffins are reacted with sulfur dioxide and chlorine in the presence of UV light to form the corresponding sulfochlorides which directly give the alkane sulfonates on hydrolysis with alkalis and the alkane sulfonic acids on reaction with water. Since di- and polysulfochlorides and  
5 chlorinated hydrocarbons can occur as secondary products of the radical reaction in the sulfochlorination process, the reaction is normally continued to conversions of only 30% and then terminated.

Another process for the production of alkane sulfonic acids is sulfoxidation in which n-paraffins are reacted with sulfur dioxide and  
10 oxygen in the presence of UV light. Successive alkyl sulfonyl radicals are formed in this radical reaction and then react with oxygen to form the alkyl persulfonyl radicals. The reaction with unreacted paraffin produces an alkyl radical and the alkyl persulfonic acid which breaks down into an alkyl peroxy sulfonyl radical and a hydroxyl radical. The reaction of the two  
15 radicals with unreacted paraffin gives the alkyl sulfonic acids and water which reacts with alkyl persulfonic acid and sulfur dioxide to form sulfuric acid. In order to keep the yield of the two end products, alkyl sulfonic acid and sulfuric acid, as high as possible and to suppress secondary reactions, this reaction is normally continued to conversions of only 1% and then  
20 terminated.

Olefin sulfonates are industrially produced by reaction of  $\alpha$ -olefins with sulfur trioxide. Zwitterions are formed as intermediate products and cyclize to form so-called sultones. Under suitable conditions (alkaline or acidic hydrolysis), these sultones react to form hydroxyalkane sulfonic  
25 acids or alkene sulfonic acids which may both also be used as anionic surfactant acids.

Alkyl benzenesulfonates as high-performance anionic surfactants have been known since the nineteen thirties. At that time, alkyl benzenes were produced by monochlorination of Kogasin fractions and subsequent  
30 Friedel-Crafts alkylation, sulfonated with oleum and neutralized with

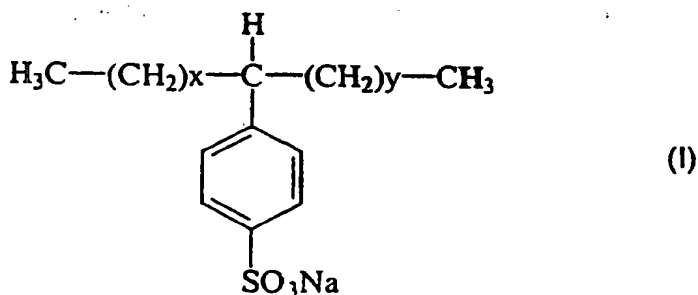
sodium hydroxide. At the beginning of the fifties, alkyl benzenesulfonates were produced by tetramerizing propylene to form branched  $\alpha$ -dodecylene and reacting the product in a Friedel-Crafts reaction using aluminium trichloride or hydrogen chloride to form tetrapropylene benzene which was then sulfonated and neutralized. This economic method of producing tetrapropylene benzene sulfonates (TPS) led to the breakthrough of this class of surfactants which subsequently displaced soaps as the main surfactant in detergents.

In view of the biological non-degradability of TPS, new alkyl benzenesulfonates distinguished by improved ecological behavior had to be produced. These requirements are satisfied by linear alkyl benzenesulfonates which, today, are virtually the only alkyl benzenesulfonates in production and which are referred to in short by the initials ABS.

Linear alkyl benzenesulfonates are prepared from linear alkyl benzenes which in turn can be obtained from linear olefins. To this end, petroleum fractions are separated using molecular sieves into the n-paraffins with the requisite purity and dehydrogenated to the n-olefins, both  $\alpha$ - and i-olefins being obtained. The olefins thus obtained are then reacted with benzene in the presence of acidic catalysts to form the alkyl benzenes, the choice of the Friedel-Crafts catalyst having an influence on the isomer distribution of the linear alkyl benzenes formed. Where aluminium trichloride is used, the content of the 2-phenyl isomers in the mixture with the 3-, 4-, 5- and other isomers is approximately 30% by weight. If, by contrast, hydrogen fluoride is used as the catalyst, the 2-phenyl isomer content can be reduced to around 20% by weight. Finally, the sulfonation of the linear alkyl benzenes is now carried out on an industrial scale with oleum, sulfuric acid or gaseous sulfur trioxide, gaseous sulfur trioxide having by far the greatest importance. Special falling-film or tube-bundle reactors are used for the sulfonation process and give as the end product a

97% by weight alkyl benzenesulfonic acid (ABSA) which may be used as the anionic surfactant acid for the purposes of the present invention.

Various salts, i.e. alkyl benzene sulfonates, can be obtained from the ABSA, depending on the choice of the neutralizing agent. For reasons of economy, it is preferred to produce and use the alkali metal salts of ABSA, preferably the sodium salts. The sodium salts correspond to general formula I:



in which the sum of x and y is normally between 5 and 13. Processes according to the invention, in which C<sub>8-16</sub>, preferably C<sub>9-13</sub> alkyl benzenesulfonic acids are used as the anionic surfactant in acid form, are preferred. Another preferred embodiment of the present invention is characterized by the use of C<sub>8-16</sub>, preferably C<sub>9-13</sub> alkyl benzenesulfonic acids derived from alkyl benzenes having a tetralin content of less than 5% by weight, based on the alkyl benzene. Another preferred embodiment is characterized by the use of alkyl benzenesulfonic acids of which the alkyl benzenes have been produced by the HF process, so that the C<sub>8-16</sub>, preferably C<sub>9-13</sub> alkyl benzene sulfonic acids used have a 2-phenyl isomer content below 22% by weight, based on the alkyl benzenesulfonic acid.

The anionic surfactants in their acid form mentioned above may be used and foamed either individually or in the form of mixtures with one another in the process according to the invention. However, it is also possible and preferred to add other, preferably acidic, detergent ingredients

in quantities of 0.1 to 40% by weight, preferably 1 to 15% by weight and more preferably 2 to 10% by weight, based on the weight of the mixture to be foamed, to the anionic surfactant in acid form before foaming.

According to the invention, preferred processes are characterized in  
5 that the surfactant-containing flowable component contains alkyl benzenesulfonic acid in quantities of 20 to 99% by weight, preferably 30 to 95% by weight and more preferably 40 to 90% by weight, based on the surfactant-containing component.

Besides the "surfactant acids", the above-mentioned fatty acids,  
10 phosphonic acids, polymer acids or partly neutralized polymer acids and "builder acids" and "complex builder acids" (particulars given hereinafter), either individually or in the form of mixtures, are also suitable acidic reactants for the purposes of the invention. Suitable detergent ingredients, which may be added to the anionic surfactant acid before foaming, are  
15 above all acidic detergent ingredients, i.e. for example phosphonic acids which, in neutralized form (phosphonates), are present as incrustation inhibitors in many detergents. According to the invention, (partly neutralized) polymer acids, such as polyacrylic acids for example, may also be used. However, acid-stable ingredients may also be mixed with the  
20 anionic surfactant acid before foaming. Suitable ingredients of this type are, for example, so-called minor components which would otherwise have to be added in expensive additional steps, i.e. for example optical brighteners, dyes etc., acid stability having to be tested in each individual case.

25 In preferred processes, the surfactant-containing flowable component additionally contains fatty acids and/or soaps in quantities of 1 to 30% by weight, preferably 2 to 25% by weight and more preferably 5 to 20% by weight, based on the surfactant-containing component.

Nonionic surfactants may optionally be added to the anionic  
30 surfactant in acid form before foaming in quantities of 0.1 to 60% by weight,

preferably 0.5 to 55% by weight and more preferably 2.5 to 10% by weight, based on the weight of the mixture to be foamed. This addition can improve the physical properties of the anionic surfactant acid foam and can eliminate the need for nonionic surfactants to be subsequently incorporated in the surfactant granules or in the detergent as a whole. The various representatives from the group of nonionic surfactants are described further below. In preferred processes, the surfactant-containing flowable component additionally contains nonionic surfactant(s) in quantities of 1 to 50% by weight, preferably 2 to 40% by weight and more preferably 5 to 30% by weight, based on the surfactant-containing component.

Preferred nonionic surfactants are alkoxylated, advantageously ethoxylated, more especially primary alcohols preferably containing 8 to 18 carbon atoms and, on average, 1 to 12 moles of ethylene oxide (EO) per mole of alcohol, in which the alcohol radical may be linear or, preferably, methyl-branched in the 2-position or may contain linear and methyl-branched radicals in the form of the mixtures typically present in oxoalcohol radicals. However, alcohol ethoxylates containing linear radicals of alcohols of native origin with 12 to 18 carbon atoms, for example coconut, palm, tallow or oleyl alcohol, and on average 2 to 8 EO per mole of alcohol are particularly preferred. Preferred ethoxylated alcohols include, for example, C<sub>12-14</sub> alcohols containing 3 EO or 4 EO, C<sub>9-11</sub> alcohol containing 7 EO, C<sub>13-15</sub> alcohols containing 3 EO, 5 EO, 7 EO or 8 EO, C<sub>12-18</sub> alcohols containing 3 EO, 5 EO or 7 EO and mixtures thereof, such as mixtures of C<sub>12-14</sub> alcohol containing 3 EO and C<sub>12-18</sub> alcohol containing 5 EO. The degrees of ethoxylation mentioned represent statistical mean values which, for a special product, can be a whole number or a broken number. Preferred alcohol ethoxylates have a narrow homolog distribution (narrow range ethoxylates, NRE). In addition to these nonionic surfactants, fatty alcohols containing more than 12 EO may also be used, examples including tallow fatty alcohol containing 14 EO, 25 EO, 30 EO or 40 EO.

The use of alkoxylated nonionic surfactants is preferred for the purposes of the invention. Process variants in which the surfactant-containing flowable component contains alkoxylated, preferably ethoxylated nonionic surfactants in quantities of 20 to 90% by weight, preferably 30 to 85% by weight and more preferably 40 to 80% by weight, based on the surfactant-containing component, have advantages, particularly preferred processes being characterized in that the surfactant-containing flowable component contains the reaction products of C<sub>8-22</sub> fatty alcohols, preferably C<sub>12-20</sub> fatty alcohols and more preferably C<sub>14-18</sub> fatty alcohols with 1 to 30 moles ethylene oxide, preferably 2 to 20 moles ethylene oxide and more preferably 5 to 10 moles ethylene oxide in quantities of 10 to 80% by weight, preferably 20 to 70% by weight and more preferably 30 to 70% by weight, based on the surfactant-containing component.

Another class of preferred nonionic surfactants which may be used either as sole nonionic surfactant or in combination with other nonionic surfactants are alkoxylated, preferably ethoxylated or propoxylated, fatty acid alkyl esters preferably containing 1 to 4 carbon atoms in the alkyl chain, more especially the fatty acid methyl esters which are described, for example, in Japanese patent application JP 58/217598 or which are preferably produced by the process described in International patent application WO-A-90/13533.

Another class of nonionic surfactants which may be used with advantage are the alkyl polyglycosides (APGs). Suitable alkyl polyglycosides correspond to the general formula RO(G)<sub>z</sub> where R is a linear or branched, more particularly 2-methyl-branched, saturated or unsaturated aliphatic radical containing 8 to 22 and preferably 12 to 18 carbon atoms and G stands for a glucose unit containing 5 or 6 carbon atoms, preferably glucose. The degree of glycosidation z is between 1.0 and 4.0, preferably between 1.0 and 2.0 and more preferably between 1.1 and 1.4.



Linear alkyl polyglucosides, i.e. alkyl polyglycosides in which the polyglycosyl moiety is a glucose unit and the alkyl moiety is an n-alkyl group, are preferably used.

The surfactant granules produced in accordance with the invention  
 5 may preferably contain alkyl polyglycosides, APG contents in the granules of more than 0.2% by weight, based on the granules as a whole, being preferred. Particularly preferred surfactant granules contain APG in quantities of 0.2 to 10% by weight, preferably 0.2 to 5% by weight and more preferably 0.5 to 3% by weight.

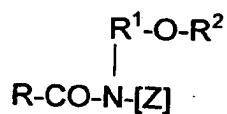
10 Nonionic surfactants of the amine oxide type, for example N-cocoalkyl-N,N-dimethylamine oxide and N-tallowalkyl-N,N-dihydroxyethylamine oxide, and the fatty acid alkanolamide type are also suitable. The quantity in which these nonionic surfactants are used is preferably no more than the quantity in which the ethoxylated fatty alcohols are used and,  
 15 more preferably, no more than half that quantity.

Other suitable surfactants are polyhydroxyfatty acid amides corresponding to formula (I):



in which RCO is an aliphatic acyl group containing 6 to 22 carbon atoms, R<sup>1</sup> is hydrogen, an alkyl or hydroxyalkyl group containing 1 to 4 carbon  
 25 atoms and [Z] is a linear or branched polyhydroxyalkyl group containing 3 to 10 carbon atoms and 3 to 10 hydroxyl groups. The polyhydroxyfatty acid amides are known substances which may normally be obtained by reductive amination of a reducing sugar with ammonia, an alkylamine or an alkanolamine and subsequent acylation with a fatty acid, a fatty acid alkyl  
 30 ester or a fatty acid chloride.

The group of polyhydroxyfatty acid amides also includes compounds corresponding to formula (II):



(II)

- 5 in which R is a linear or branched alkyl or alkenyl group containing 7 to 12 carbon atoms, R<sup>1</sup> is a linear, branched or cyclic alkyl group or an aryl group containing 2 to 8 carbon atoms and R<sup>2</sup> is a linear, branched or cyclic alkyl group or an aryl group or an oxyalkyl group containing 1 to 8 carbon atoms, C<sub>1-4</sub> alkyl or phenyl groups being preferred, and [Z] is a linear polyhydroxy-  
 10 alkyl group, of which the alkyl chain is substituted by at least two hydroxyl groups, or alkoxyated, preferably ethoxyated or propoxyated, derivatives of that group.

[Z] is preferably obtained by reductive amination of a reduced sugar, for example glucose, fructose, maltose, lactose, galactose, mannose or  
 15 xylose. The N-alkoxy- or N-aryloxy-substituted compounds may then be converted into the required polyhydroxyfatty acid amides by reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst, for example in accordance with the teaching of International patent application WO-A-95/07331.

- 20 In preferred processes according to the invention, the surfactant-containing flowable component contains alkoxyated, preferably ethoxyated, nonionic surfactants, preferably the reaction products of C<sub>8-22</sub> fatty alcohols, preferably C<sub>12-20</sub> fatty alcohols and more preferably C<sub>14-18</sub> fatty alcohols with 1 to 30 moles ethylene oxide, preferably with 2 to 20 moles  
 25 ethylene oxide and more preferably with 5 to 10 moles ethylene oxide.

According to the invention, the surfactant-containing flowable component may consist entirely of one or more surfactants and, hence, may be free from non-surfactant compounds. According to the invention, however, other ingredients of detergents may be incorporated in the surfac-  
 30 tant-containing component. Besides active substances, the surfactant-containing component may also contain water from its production. This

water may also be added to adjust favorable viscosity values or to optimize the foaming of the surfactant-containing component. In preferred processes, however, the surfactant-containing flowable component contains less than 20% by weight, preferably less than 15% by weight and more preferably less than 10% by weight of water, based on the surfactant-containing component.

So-called "minor components" in particular may advantageously be introduced into the surfactant granules through the foam serving as granulation liquid in the process according to the invention. In preferred processes according to the invention, the surfactant-containing flowable component contains other detergent ingredients, more particularly substances from the group of complexing agents, polymers, optical brighteners, dyes and perfumes and alkalis. These minor components, which are preferably added to the surfactant-containing flowable component, are described hereinafter.

The foaming of the flowable surfactant-containing component may be carried out at room temperature or with cooling or heating, depending on the desired properties of the foam. Preferred variants of the process are carried out in such a way that the surfactant-containing flowable component to be foamed has temperatures before foaming in the range from 20 to 120°C, preferably in the range from 30 to 90°C and more preferably in the range from 50 to 75°C. The viscosity of the surfactant-containing component may be varied within wide limits through the choice of the ingredients, relatively low-viscosity surfactant-containing components generally giving less stable foams.

As mentioned above, one advantage of the process according to the invention is that, in contrast to conventional granulation processes, high-viscosity granulation liquids can also be used. Thus, surfactant-containing liquid components with viscosities above 100 mPas may be used in the process according to the invention, although liquid components with

viscosities above 1000 mPas and even as high as 5000 mPas may also be foamed in accordance with the invention and readily used as a granulation aid in the form of the "granulation foam".

5 The flowable surfactant-containing component is foamed by the gaseous medium to form a foam. The liquid and the gaseous medium may be used in varying quantities and ratios to one another. From the point of view of process technology, the gaseous medium is preferably used in quantities of at least 20% by volume, based on the quantity of liquid to be foamed, for foam generation.

10 If, therefore, 1 liter of a surfactant-containing component for example is to be foamed, at least 200 ml of gaseous medium are preferably used for foaming. In preferred processes, the amount of gaseous medium is well above that value, so that processes in which the quantity of gas used for foaming is one to three hundred times, preferably five to two hundred times  
15 and more preferably ten to one hundred times the volume of the quantity of liquid to be foamed are preferred. As mentioned above, air is preferably used as the gaseous medium. However, other gases or gas mixtures may be used for foaming. For example, it may be preferred to pass air or oxygen-enriched air through an ozonizer before the gas is used for  
20 foaming. Gas mixtures containing 0.1 to 4% by weight of ozone, for example, may be prepared in this way. The ozone content of the foaming gas leads to the oxidative destruction of unwanted constituents in the liquids to be foamed. The addition of ozone can have a distinct lightening effect, particularly in the case of partly discolored anionic surfactant acids.

25 Accordingly, preferably 1 to 300 liters, more preferably 5 to 200 liters and most preferably 10 to 100 liters of air are used to foam the liter of surfactant-containing component mentioned by way of example above.

On the other hand, the temperature of the foam formed can be controlled through the temperature of the liquid to be foamed on the one  
30 hand and the temperature of the gaseous medium on the other hand. In

preferred variants of the process according to the invention, the foam formed has temperatures below 115°C, preferably between 20 and 80°C and more preferably between 30 and 70°C.

5 The foam formed, which is used as a granulation aid in the next step of the process, can be characterized by other physical parameters. For example, the foam preferably has a density below 0.80 g/cm<sup>3</sup>, preferably in the range from 0.10 to 0.6 g/cm<sup>3</sup> and more preferably in the range from 0.30 to 0.55 g/cm<sup>3</sup>. In another preferred embodiment, the foam has mean pore sizes below 10 mm, preferably below 5 mm and more preferably  
10 below 2 mm.

The above-mentioned physical parameters of temperature, density and mean pore size characterize the foam at the time it is formed. However, the process is preferably controlled in such a way that the foam satisfies the above-mentioned criteria even at the time it is introduced into  
15 the mixer.

Process control strategies in which the foam satisfies only one or two of the criteria mentioned when introduced into the mixer are possible, although both the temperature and the density and pore size preferably lie within the ranges mentioned when the foam enters the mixer.

20 After its formation, the foam is applied to a bed of solids initially introduced into a mixer where it serves as a granulation aid. This step of the process may be carried out in various mixers and granulators, as described in detail hereinafter. The solid bed introduced into the mixer may contain all the substances used in detergents. In this way, ready-to-  
25 use detergents can be produced by the process according to the invention. Normally, however, certain detergent ingredients are not included in the granulation process in order to prevent these ingredients from entering into unwanted reactions with one another under the mechanical influence of the granulating tools. Ingredients which are normally added to the surfactant  
30 granules in a subsequent step, i.e. after the granulation process, include,

for example bleaching agents, bleach activators, enzymes and foam inhibitors.

Besides the surfactant, the surfactant granules produced in accordance with the invention preferably contain substances which function  
5 as active substances in the final detergent. In preferred processes, therefore, the bed of solids introduced into the mixer contains one or more substances from the group of builders, more especially alkali metal carbonates, sulfates and silicates, zeolites and polymers.

In order to produce surfactant granules which can be subsequently  
10 mixed with other components to form the final detergent without any unwanted reactions occurring, the surfactant granules preferably do not contain any residues of excess anionic surfactant acid(s). This can readily be achieved through the presence in the bed of solids introduced into the mixer of alkaline constituents which neutralize the anionic surfactant acids.  
15 Such constituents include, in particular, carbonates and hydrogen carbonates, although other alkaline components, such as oxides, hydroxides, etc., and organic neutralizing agents, such as amines, etc. may also be used. In preferred processes according to the invention, the bed of solids introduced into the mixer contains one or more substances from the  
20 group of alkali metal carbonates and/or hydrogen carbonates, preferably sodium carbonate, in a quantity sufficient to neutralize the quantity of acid introduced through the foam.

In one particularly preferred embodiment, the bed of solids introduced into the mixer contains the alkaline components in a quantity  
25 sufficient to neutralize the quantity of acid introduced through the foam. If, for example, 2 moles of monobasic acid are introduced through the foam containing anionic surfactant acid, at least 2 neutralization equivalents, i.e. for example 2 moles NaOH or 1 mole sodium carbonate, should be present in the bed of solids. Processes according to the invention in which the bed  
30 of solids contains more than the quantity of bases stoichiometrically

necessary for neutralizing the quantity of acid introduced are preferred. In a particularly preferred embodiment, the bed of solids contains more than twice, preferably more than three times, more preferably more than four time and most preferably more than five times the amount of alkalinity  
5 required to neutralize the quantity of acid introduced through the foam

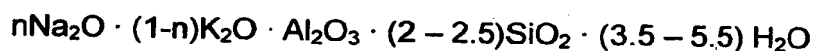
Besides the deterative substances, builders are the most important ingredients of detergents. In the process according to the invention, any of the builders typically used in detergents may be present in the solid bed, i.e. in particular zeolites, silicates, carbonates, organic co-builders and -  
10 providing there are no ecological objections to their use - also phosphates.

Suitable crystalline layer-form sodium silicates correspond to the general formula  $\text{Na}_2\text{MSi}_x\text{O}_{2x+1}y \cdot \text{H}_2\text{O}$ , where M is sodium or hydrogen, x is a number of 1.9 to 4 and y is a number of 0 to 20, preferred values for x being 2, 3 or 4. Crystalline layer silicates such as these are described, for  
15 example, in European patent application **EP-A-0 164 514**. Preferred crystalline layer silicates corresponding to the above formula are those in which M is sodium and x assumes the value 2 or 3. Both - and -sodium disilicates  $\text{Na}_2\text{Si}_2\text{O}_5 \cdot y \text{H}_2\text{O}$  are particularly preferred, -sodium disilicate being obtainable, for example, by the process described in  
20 International patent application **WO-A- 91/08171**.

Other useful builders are amorphous sodium silicates with a modulus ( $\text{Na}_2\text{O}:\text{SiO}_2$  ratio) of 1:2 to 1:3.3, preferably 1:2 to 1:2.8 and more preferably 1:2 to 1:2.6 which dissolve with delay and exhibit multiple wash cycle properties. The delay in dissolution in relation to conventional  
25 amorphous sodium silicates can have been obtained in various ways, for example by surface treatment, compounding, compacting or by overdrying. In the context of the invention, the term "amorphous" is also understood to encompass "X-ray amorphous". In other words, the silicates do not produce any of the sharp X-ray reflexes typical of crystalline substances in  
30 X-ray diffraction experiments, but at best one or more maxima of the

scattered X-radiation which have a width of several degrees of the diffraction angle. However, particularly good builder properties may even be achieved where the silicate particles produce crooked or even sharp diffraction maxima in electron diffraction experiments. This may be  
 5 interpreted to mean that the products have microcrystalline regions between 10 and a few hundred nm in size, values of up to at most 50 nm and, more particularly, up to at most 20 nm being preferred. So-called X-ray amorphous silicates such as these, which also dissolve with delay in relation to conventional waterglasses, are described for example in  
 10 German patent application **DE-A-44 00 024**. Compacted amorphous silicates, compounded amorphous silicates and overdried X-ray-amorphous silicates are particularly preferred.

The finely crystalline, synthetic zeolite containing bound water used in accordance with the invention is preferably zeolite A and/or zeolite P.  
 15 Zeolite MAP® (Crosfield) is a particularly preferred P-type zeolite. However, zeolite X and mixtures of A, X and/or P are also suitable. According to the invention, it is also possible to use, for example, a commercially obtainable co-crystallizate of zeolite X and zeolite A (ca. 80% by weight zeolite X) which is marketed by CONDEA Augusta S.p.A. under  
 20 the name of VEGOGOND AX® and which may be described by the following formula:



25 Suitable zeolites have a mean particle size of less than 10  $\mu\text{m}$  (volume distribution, as measured by the Coulter Counter Method) and contain preferably 18 to 22% by weight and more preferably 20 to 22% by weight of bound water.

The generally known phosphates may of course also be used as  
 30 builders providing their use should not be avoided on ecological grounds.



Of the large number of commercially obtainable phosphates, alkali metal phosphates have the most importance in the detergent industry, pentasodium and pentapotassium phosphate (sodium and potassium tripolyphosphate) being particularly preferred.

5        "Alkali metal phosphates" is the collective term for the alkali metal (more particularly sodium and potassium) salts of the various phosphoric acids, including metaphosphoric acids  $(\text{HPO}_3)_n$  and orthophosphoric acid  $(\text{H}_3\text{PO}_4)$  and representatives of higher molecular weight. The phosphates combine several advantages: they act as alkalinity sources, prevent lime  
10 deposits on machine parts and lime incrustations in fabrics and, in addition, contribute towards the cleaning effect.

Sodium dihydrogen phosphate  $(\text{NaH}_2\text{PO}_4)$  exists as the dihydrate (density  $1.91 \text{ g/cm}^3$ , melting point  $60^\circ$ ) and as the monohydrate (density  $2.04 \text{ g/cm}^3$ ). Both salts are white readily water-soluble powders which, on  
15 heating, lose the water of crystallization and, at  $200^\circ$ , are converted into the weakly acidic diphosphate (disodium hydrogen diphosphate,  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ ) and, at higher temperatures, into sodium trimetaphosphate  $(\text{Na}_3\text{P}_3\text{O}_9)$  and Maddrell's salt (see below).  $\text{NaH}_2\text{PO}_4$  shows an acidic reaction. It is formed by adjusting phosphoric acid with sodium hydroxide to a pH value  
20 of 4.5 and spraying the resulting "mash". Potassium dihydrogen phosphate (primary or monobasic potassium phosphate, potassium biphosphate, KDP),  $\text{KH}_2\text{PO}_4$ , is a white salt with a density of  $2.33 \text{ g/cm}^3$ , has a melting point of  $253^\circ$  [decomposition with formation of potassium polyphosphate  $(\text{KPO}_3)_x$ ] and is readily soluble in water.

25        Disodium hydrogen phosphate (secondary sodium phosphate),  $\text{Na}_2\text{HPO}_4$ , is a colorless, readily water-soluble crystalline salt. It exists in water-free form and with 2 moles (density  $2.066 \text{ g/cm}^3$ , water loss at  $95^\circ$ ), 7 moles (density  $1.68 \text{ g/cm}^3$ , melting point  $48^\circ$  with loss of 5  $\text{H}_2\text{O}$ ) and 12 moles of water (density  $1.52 \text{ g/cm}^3$ , melting point  $35^\circ$  with loss of 5  $\text{H}_2\text{O}$ ),  
30 becomes water-free at  $100^\circ$  and, on fairly intensive heating, is converted

into the diphosphate  $\text{Na}_4\text{P}_2\text{O}_7$ . Disodium hydrogen phosphate is prepared by neutralization of phosphoric acid with soda solution using phenolphthalein as indicator. Dipotassium hydrogen phosphate (secondary or dibasic potassium phosphate),  $\text{K}_2\text{HPO}_4$ , is an amorphous white salt which is readily soluble in water.

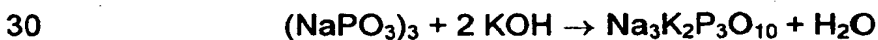
Trisodium phosphate, tertiary sodium phosphate,  $\text{Na}_3\text{PO}_4$ , consists of colorless crystals which have a density of  $1.62 \text{ g/cm}^3$  and a melting point of  $73-76^\circ$  (decomposition) as the dodecahydrate, a melting point of  $100^\circ$  as the decahydrate (corresponding to 19-20%  $\text{P}_2\text{O}_5$ ) and a density of  $2.536 \text{ g/cm}^3$  in water-free form (corresponding to 39-40%  $\text{P}_2\text{O}_5$ ). Trisodium phosphate is readily soluble in water through an alkaline reaction and is prepared by concentrating a solution of exactly 1 mole of disodium phosphate and 1 mole of  $\text{NaOH}$  by evaporation. Tripotassium phosphate (tertiary or tribasic potassium phosphate),  $\text{K}_3\text{PO}_4$ , is a white deliquescent granular powder with a density of  $2.56 \text{ g/cm}^3$ , has a melting of  $1340^\circ$  and is readily soluble in water through an alkaline reaction. It is formed, for example, when Thomas slag is heated with coal and potassium sulfate. Despite their higher price, the more readily soluble and therefore highly effective potassium phosphates are often preferred to corresponding sodium compounds in the detergent industry.

Tetrasodium diphosphate (sodium pyrophosphate),  $\text{Na}_4\text{P}_2\text{O}_7$ , exists in water-free form (density  $2.534 \text{ g/cm}^3$ , melting point  $988^\circ$ , a figure of  $880^\circ$  has also been mentioned) and as the decahydrate (density  $1.815 - 1.836 \text{ g/cm}^3$ , melting point  $94^\circ$  with loss of water). Both substances are colorless crystals which dissolve in water through an alkaline reaction.  $\text{Na}_4\text{P}_2\text{O}_7$  is formed when disodium phosphate is heated to  $>200^\circ$  or by reacting phosphoric acid with soda in a stoichiometric ratio and spray-drying the solution. The decahydrate complexes heavy metal salts and hardness salts and, hence, reduces the hardness of water. Potassium diphosphate (potassium pyrophosphate),  $\text{K}_4\text{P}_2\text{O}_7$ , exists in the form of the trihydrate and

is a colorless hygroscopic powder with a density of 2.33 g/cm<sup>3</sup> which is soluble in water, the pH value of a 1% solution at 25° being 10.4.

Relatively high molecular weight sodium and potassium phosphates are formed by condensation of NaH<sub>2</sub>PO<sub>4</sub> or KH<sub>2</sub>PO<sub>4</sub>. They may be divided into cyclic types, namely the sodium and potassium metaphosphates, and chain types, the sodium and potassium polyphosphates. The chain types in particular are known by various different names: fused or calcined phosphates, Graham's salt, Kurrol's salt and Maddrell's salt. All higher sodium and potassium phosphates are known collectively as condensed phosphates.

The industrially important pentasodium triphosphate, Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub> (sodium tripolyphosphate), is a non-hygroscopic white water-soluble salt which crystallizes without water or with 6 H<sub>2</sub>O and which has the general formula NaO-[P(O)(ONa)-O]<sub>n</sub>-Na where n = 3. Around 17 g of the salt free from water of crystallization dissolve in 100 g of water at room temperature, around 20 g at 60° and around 32 g at 100°. After heating of the solution for 2 hours to 100°, around 8% orthophosphate and 15% diphosphate are formed by hydrolysis. In the preparation of pentasodium triphosphate, phosphoric acid is reacted with soda solution or sodium hydroxide in a stoichiometric ratio and the solution is spray-dried. Similarly to Graham's salt and sodium diphosphate, pentasodium triphosphate dissolves many insoluble metal compounds (including lime soaps, etc.). Pentapotassium triphosphate, K<sub>5</sub>P<sub>3</sub>O<sub>10</sub> (potassium tripolyphosphate), is marketed for example in the form of a 50% by weight solution (> 23% P<sub>2</sub>O<sub>5</sub>, 25% K<sub>2</sub>O). The potassium polyphosphates are widely used in the detergent industry. Sodium potassium tripolyphosphates, which may also be used in accordance with the invention, also exist. They are formed for example when sodium trimetaphosphate is hydrolyzed with KOH:



According to the invention, they may be used in exactly the same way as sodium tripolyphosphate, potassium tripolyphosphate or mixtures thereof. Mixtures of sodium tripolyphosphate and sodium potassium tripolyphosphate or mixtures of potassium tripolyphosphate and sodium potassium tripolyphosphate or mixtures of sodium tripolyphosphate and potassium tripolyphosphate and sodium potassium tripolyphosphate may also be used in accordance with the invention.

In particular, polycarboxylates/polycarboxylic acids, polymeric polycarboxylates, aspartic acid, polyacetals, dextrans, other organic cobuilders (see below) and phosphonates may be used as organic cobuilders in the process according to the invention as part of the bed of solids. These classes of substance are described in the following.

Useful organic builders are, for example, the polycarboxylic acids usable in the form of their sodium salts, such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids, aminocarboxylic acids, nitrilotriacetic acid (NTA), providing there are no ecological objections to its use, and mixtures of these acids. Preferred salts are the salts of the polycarboxylic acids, such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids and mixtures thereof.

The acids per se may also be used. Besides their builder effect, the acids typically have the property of an acidifying component and, accordingly, are also used to establish a lower and more mild pH value in laundry or dishwashing detergents. Citric acid, succinic acid, glutaric acid, adipic acid, gluconic acid and mixtures thereof are particularly mentioned in this regard.

Other suitable builders are polymeric polycarboxylates such as, for example, the alkali metal salts of polyacrylic acid or polymethacrylic acid, for example those having a relative molecular weight of 500 to 70,000 g/mole.

The molecular weights mentioned in this specification for polymeric

polycarboxylates are weight-average molecular weights  $M_w$  of the particular acid form which, basically, were determined by gel permeation chromatography (GPC) using a UV detector. The measurement was carried out against an external polyacrylic acid standard which provides realistic molecular weight values by virtue of its structural similarity to the polymers investigated. These values differ distinctly from the molecular weights measured against polystyrene sulfonic acids as standard. The molecular weights measured against polystyrene sulfonic acids are generally far higher than the molecular weights mentioned in this specification.

Suitable polymers are, in particular, polyacrylates which preferably have a molecular weight of 2,000 to 20,000 g/mole. By virtue of their superior solubility, preferred representatives of this group are the short-chain polyacrylates which have molecular weights of 2,000 to 10,000 g/mole and, more particularly, 3,000 to 5,000 g/mole.

Also suitable are copolymeric polycarboxylates, particularly those of acrylic acid with methacrylic acid and those of acrylic acid or methacrylic acid with maleic acid. Acrylic acid/maleic acid copolymers containing 50 to 90% by weight of acrylic acid and 50 to 10% by weight of maleic acid have proved to be particularly suitable. Their relative molecular weight, based on the free acids, is generally in the range from 2,000 to 70,000 g/mole, preferably in the range from 20,000 to 50,000 g/mole and more preferably in the range from 30,000 to 40,000 g/mole.

The (co)polymeric polycarboxylates may be used either in powder form or in the form of an aqueous solution. The content of (co)polymeric polycarboxylates in the compositions is preferably between 0.5 and 20% by weight and more preferably between 3 and 10% by weight.

In order to improve their solubility in water, the polymers may also contain allyl sulfonic acids, for example allyloxybenzenesulfonic acid and methallyl sulfonic acid as monomer.

Biodegradable polymers of more than two different monomer units are also particularly preferred, examples including those which contain salts of acrylic acid and maleic acid and vinyl alcohol or vinyl alcohol derivatives as monomers or those which contain salts of acrylic acid and 2-alkylallyl sulfonic acid and sugar derivatives as monomers.

Other preferred copolymers are those described in German patent applications **DE-A-43 03 320** and **DE-A-44 17 734** which preferably contain acrolein and acrylic acid/acrylic acid salts or acrolein and vinyl acetate as monomers.

Other preferred builders are polymeric aminodicarboxylic acids, salts or precursors thereof. Polyaspartic acids or salts and derivatives thereof which, according to German patent application **DE-A-195 40 086**, have a bleach-stabilizing effect in addition to their co-builder properties are particularly preferred.

Other suitable builders are polyacetals which may be obtained by reaction of dialdehydes with polyol carboxylic acids containing 5 to 7 carbon atoms and at least three hydroxyl groups. Preferred polyacetals are obtained from dialdehydes, such as glyoxal, glutaraldehyde, terephthalaldehyde and mixtures thereof and from polyol carboxylic acids, such as gluconic acid and/or glucoheptonic acid.

Other suitable organic builders are dextrans, for example oligomers or polymers of carbohydrates which may be obtained by partial hydrolysis of starches. The hydrolysis may be carried out by standard methods, for example acid- or enzyme-catalyzed methods. The end products are preferably hydrolysis products with average molecular weights of 400 to 500,000 g/mole. A polysaccharide with a dextrose equivalent (DE) of 0.5 to 40 and, more particularly, 2 to 30 is preferred, the DE being an accepted measure of the reducing effect of a polysaccharide by comparison with dextrose which has a DE of 100. Both maltodextrins with a DE of 3 to 20 and dry glucose syrups with a DE of 20 to 37 and also so-called yellow

dextrins and white dextrins with relatively high molecular weights of 2,000 to 30,000 g/mole may be used.

The oxidized derivatives of such dextrins are their reaction products with oxidizing agents which are capable of oxidizing at least one alcohol  
5 function of the saccharide ring to the carboxylic acid function. Dextrins thus oxidized and processes for their production are known, for example, from European patent applications EP-A-0 232 202, EP-A-0 427 349, EP-A-0 472 042 and EP-A-0 542 496 and from International patent applications WO 92/18542, WO 93/08251, WO 93/16110, WO 94/28030,  
10 WO 95/07303, WO 95/12619 and WO 95/20608. An oxidized oligosaccharide according to German patent application DE-A-196 00 018 is also suitable. A product oxidized at C<sub>6</sub> of the saccharide ring can be particularly advantageous.

Other suitable co-builders are oxydisuccinates and other derivatives  
15 of disuccinates, preferably ethylenediamine disuccinate. Ethylenediamine-N,N'-disuccinate (EDDS) is preferably used in the form of its sodium or magnesium salts. Glycerol disuccinates and glycerol trisuccinates are also particularly preferred in this connection. The quantities used in zeolite-containing and/or silicate-containing formulations are from 3 to 15% by  
20 weight.

Other useful organic co-builders are, for example, acetylated hydroxycarboxylic acids and salts thereof which may optionally be present in lactone form and which contain at least 4 carbon atoms, at least one hydroxy group and at most two acid groups. Co-builders such as these are  
25 described, for example, in International patent application WO-A-95/20029.

Another class of substances with co-builder properties are the phosphonates, more particularly hydroxyalkane and aminoalkane phosphonates. Among the hydroxyalkane phosphonates, 1-hydroxyethane-1,1-diphosphate (HEDP) is particularly important as a co-builder. It is  
30 preferably used in the form of a sodium salt, the disodium salt showing a

neutral reaction and the tetrasodium salt an alkaline ration (pH 9). Preferred aminoalkane phosphonates are ethylenediamine tetramethylene phosphonate (EDTMP), diethylenetriamine pentamethylene phosphonate (DTPMP) and higher homologs thereof. They are preferably used in the form of the neutrally reacting sodium salts, for example as the hexasodium salt of EDTMP and as the hepta- and octasodium salt of DTPMP. Within the class of phosphonates, HEDP is preferably used as builder. The aminoalkane phosphonates also show a pronounced heavy metal binding capacity. Accordingly, it can be of advantage, particularly where the detergents also contain bleaching agents, to use aminoalkane phosphonates, more especially DTPMP, or mixtures of the phosphonates mentioned.

In addition, any compounds capable of forming complexes with alkaline earth metal ions may be used as co-builders.

The bed of solids introduced into the mixer may also contain compounded raw materials, i.e. ingredients which are themselves end products of previous process steps. Besides granulated, compacted or extruded raw materials, spray-dried basic powders are also suitable as a constituent of the bed of solids introduced into the mixer. These spray-dried basic powders may be surfactant-free (for example polymer compounds), although they preferably contain surfactants. If spray-dried basic powders such as these are to be used, the bed of solids introduced into the mixer contains the spray-dried basic powders, preferably the surfactant-containing spray-dried basic powders, in quantities based on the solids introduced into the mixer of 10 to 60% by weight, preferably 15 to 30% by weight and more preferably 20 to 60% by weight in preferred variants of the process.

Surfactant granules are formed by addition of the foam under the effect of the mixing tools. Preferred processes according to the invention are characterized in that the surfactant foam is added to the bed of solids



introduced into the mixer in a ratio by weight of foam to solids to 1:100 to 9:1, preferably 1:30 to 2:1 and more preferably 1:20 to 1:1. Optimal granulation results are obtained with the preferred quantities of granulation aid (surfactant foam).

5       As already mentioned, the process according to the invention may be carried out in various conventional mixers and granulators. Mixers suitable for carrying out the process according to the invention are, for example, Series R or RV Eirich® mixers (trademarks of Maschinenfabrik Gustav Eirich, Hardheim), the Schugi® Flexomix, Fukae® FS-G mixers  
10 (trademarks of Fukae Powtech, Kogyo Co., Japan), Lödige® FM, KM and CB mixers (trademarks of Lödige Maschinenbau GmbH, Paderborn) or Series T or K-T Drais® mixers (trademarks of Drais-Werke GmbH, Mannheim). Some preferred embodiments of the process according to the invention are described in the following.

15       For example, it is possible and preferred to carry out the process according to the invention in a low-speed mixer/granulator at peripheral speeds of the tools of 2 m/s to 7 m/s, the foam containing anionic surfactant acid being added to the bed of solids in the mixer over a period of 0.5 to 10 minutes, preferably over a period of 1 to 7 minutes and more  
20 preferably over a period of 2 to 5 minutes.

Alternatively, in preferred variants of the process, the foam containing anionic surfactant acid may be added to the bed of solids in the mixer in a high-speed mixer/granulator over a period of 0.1 to 30 seconds, preferably up to 10 seconds and more preferably between 0.5 and 2  
25 seconds at peripheral speeds of 8 m/s to 35 m/s.

Whereas the two process variants described above each use a mixer, it is also possible in accordance with the invention to combine two mixers with one another. For example, preferred processes are characterized in that the foam containing anionic surfactant acid is added to an  
30 agitated bed of solids in a first low-speed mixer/granulator, 40 to 100% by

weight, based on the total quantity of constituents used, of the solid and liquid constituents being pregranulated and the "pregranules" from the first process step optionally being mixed with the remaining solid and/or liquid constituents and converted into granules in a second high-speed mixer/

5 granulator. In this variant of the process, the foam containing anionic surfactant acid is added to a bed of solids in a first mixer/granulator and the mixture is pregranulated. The composition of the foam and of the bed of solids introduced into the first mixer are selected so that 40 to 100% by weight, preferably 50 to 90% by weight and more preferably 60 to 80% by

10 weight of the solid and liquid constituents, based on the total quantity of constituents used, are contained in the "pregranules". These "pregranules" are then mixed with more solids in the second mixer and granulated in the presence of more liquid components to form the final surfactant granules. According to the invention, the liquid constituents may advantageously

15 serve as a granulation aid ("granulation liquid") in the form of a foam in the second process step also, rather than being sprayed on as a liquid. The composition of the foam added to the second mixer may differ from the composition of the foam used in the first mixer, so that preferred processes described in the foregoing are characterized in that the pregranules from

20 the first process step are granulated to form the final granules in the second high-speed mixer/granulator, again in the presence of a surfactant-containing foam which may differ in its composition from the foam used in the first process step. The second foam may of course be free from anionic surfactant acids.

25 According to the invention, the above-mentioned sequence of low-speed/high-speed mixers may also be reversed, resulting in a process according to the invention in which the foam containing anionic surfactant acid is added to an agitated bed of solids in a first high-speed mixer/granulator, 40 to 100% by weight, based on the total quantity of constituents

30 used, of the solid and liquid constituents being pregranulated and the

pregranules from the first process step optionally being mixed with the remaining solid and/or liquid constituents and converted into granules in a second low-speed mixer/granulator.

5 The foregoing observations apply equally to this variant of the process, so that here, too, preferred processes are characterized in that the pregranules from the first step of the process are granulated to form the final granules in the second low-speed mixer/granulator, again in the presence of a foam containing anionic surfactant acid which may differ in its composition from the foam used in the first step of the process.

10 All the variants of the process according to the invention described in the foregoing may be carried out either in batches or continuously. High-speed mixer/granulators are used in some of the above-described variants of the process according to the invention. In one particularly preferred embodiment of the invention, a mixer comprising both a mixing unit and a  
15 size-reducing unit is used as a high-speed mixer, the mixing shaft being driven at peripheral speeds of 50 to 150 r.p.m. and preferably 60 to 80 r.p.m. and the shaft of the size-reducing unit being driven at rotational speeds of 500 to 5000 r.p.m. and preferably 1000 to 300 r.p.m.

The process according to the invention is variable within wide limits  
20 in regard to the choice and concentration of the ingredients to be used. Nevertheless, it is preferred if surfactant granules with surfactant contents above 10% by weight, preferably above 15% by weight and more preferably above 20% by weight, based on the granules, and bulk densities above 600 g/l, preferably above 700 g/l and more preferably above 800 g/l  
25 are produced in accordance with the invention.

The granulation process according to the invention may be carried out in such a way that particles with a predetermined particle size distribution are obtained. Preferred processes according to the invention are characterized in that the surfactant granules have a particle size  
30 distribution where at least 50% by weight, preferably at least 60% by

weight and more preferably at least 70% by weight of the particles are between 400 and 1600  $\mu\text{m}$  in size. The residual moisture content of the surfactant granules produced in accordance with the invention can also be predetermined through the choice of the raw materials, so that there is no  
5 need for any subsequent drying steps. In preferred processes, the surfactant granules have residual free water contents of 2 to 15% by weight and preferably 4 to 10% by weight, based on the surfactant granules. The residual free water content may be determined, for example, by a modified UX method (Sartorius MA 30, 120°C program for 10 minutes).

10 Components for detergents which only form the final detergent after mixing with other ingredients may be produced by the process according to the invention. However, surfactant granules which, as such, actually represent a ready-to-use detergent (for example a detergent for colored fabrics) may of course also be produced in accordance with the invention.

15 The surfactant granules produced by the process according to the invention may be subsequently mixed with other detergent ingredients to form the end product. These ingredients may also be directly incorporated in the surfactant granules via the bed of solids or via the surfactant foam and are described in the following:

20 Besides the constituents mentioned (surfactant and builders), typical detergent ingredients from the group of bleaching agents, bleach activators, enzymes, pH regulators, perfumes, perfume carriers, fluorescers, dyes, foam inhibitors, silicone oils, redeposition inhibitors, optical brighteners, discoloration inhibitors, dye transfer inhibitors and  
25 corrosion inhibitors are particularly important.

Among the compounds yielding  $\text{H}_2\text{O}_2$  in water which serve as bleaching agents, sodium perborate tetrahydrate and sodium perborate monohydrate are particularly important. Other useful bleaching agents are, for example, sodium percarbonate, peroxyphosphates, citrate perhy-  
30 drates and  $\text{H}_2\text{O}_2$ -yielding peracidic salts or peracids, such as

perbenzoates, peroxophthalates, diperazelaic acid, phthaloiminoperacid or diperdodecane dioic acid. Typical organic bleaching agents are diacyl peroxides, such as dibenzoyl peroxide for example. Other typical organic bleaching agents are the peroxy acids, of which alkyl peroxy acids and aryl peroxy acids are particularly mentioned as examples. Preferred representatives are (a) peroxybenzoic acid and ring-substituted derivatives thereof, such as alkyl peroxybenzoic acids, but also peroxy- $\alpha$ -naphthoic acid and magnesium monoperphthalate, (b) aliphatic or substituted aliphatic peroxy acids, such as peroxy lauric acid, peroxy stearic acid,  $\epsilon$ -phthalimidoperoxycaproic acid [phthaloiminoperoxyhexanoic acid (PAP)], o-carboxybenzamidoperoxycaproic acid, N-nonenylamidoperadipic acid and N-nonenylamidopersuccinates. and (c) aliphatic and araliphatic peroxydicarboxylic acids, such as 1,12-diperoxycarboxylic acid, 1,9-diperoxyazelaic acid, diperoxysebacic acid, diperoxybrassylic acid, diperoxyphthalic acids, 2-decyldiperoxybutane-1,4-dioic acid, N,N-terephthaloyl-di(6-aminopercaproic acid).

Other suitable bleaching agents in compositions for dishwashing machines are chlorine- and bromine-releasing substances. Suitable chlorine- or bromine-releasing materials are, for example, heterocyclic N-bromamides and N-chloramides, for example trichloroisocyanuric acid, tribromoisocyanuric acid, dibromoisocyanuric acid and/or dichloroisocyanuric acid (DICA) and/or salts thereof with cations, such as potassium and sodium. Hydantoin compounds, such as 1,3-dichloro-5,5-dimethyl hydantoin, are also suitable.

In order to obtain an improved bleaching effect where washing is carried out at temperatures of 60°C or lower, bleach activators may be incorporated. The bleach activators may be compounds which form aliphatic peroxocarboxylic acids containing preferably 1 to 10 carbon atoms and more preferably 2 to 4 carbon atoms and/or optionally substituted perbenzoic acid under perhydrolysis conditions. Substances bearing O-

and/or N-acyl groups with the number of carbon atoms mentioned and/or optionally substituted benzoyl groups are suitable. Preferred bleach activators are polyacylated alkylenediamines, more particularly tetraacetyl ethylenediamine (TAED), acylated triazine derivatives, more particularly  
5 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, more particularly tetraacetyl glycoluril (TAGU), N-acylimides, more particularly N-nonanoyl succinimide (NOSI), acylated phenol sulfonates, more particularly n-nonanoyl or isononanoyloxybenzene-sulfonate (n- or iso-NOBS), carboxylic anhydrides, more particularly  
10 phthalic anhydride, acylated polyhydric alcohols, more particularly triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran.

In addition to or instead of the conventional bleach activators mentioned above, so-called bleach catalysts may also be incorporated. Bleach catalysts are bleach-boosting transition metal salts or transition  
15 metal complexes such as, for example, manganese-, iron-, cobalt-, ruthenium- or molybdenum-salen complexes or carbonyl complexes. Manganese, iron, cobalt, ruthenium, molybdenum, titanium, vanadium and copper complexes with nitrogen-containing tripod ligands and cobalt-, iron-, copper- and ruthenium-ammine complexes may also be used as bleach  
20 catalysts.

Suitable enzymes are those from the class of proteases, lipases, amylases, cellulases or mixtures thereof. Enzymes obtained from bacterial strains or fungi, such as *Bacillus subtilis*, *Bacillus licheniformis* and *Streptomyces griseus*, are particularly suitable. Proteases of the subtilisin  
25 type are preferred, proteases obtained from *Bacillus lentus* being particularly preferred. Enzyme mixtures, for example of protease and amylase or protease and lipase or protease and cellulase or of cellulase and lipase or of protease, amylase and lipase or of protease, lipase and cellulase, but especially cellulase-containing mixtures, are of particular  
30 interest. Peroxidases or oxidases have also proved to be suitable in some

cases. The enzymes may be adsorbed to supports and/or encapsulated in shell-forming substances to protect them against premature decomposition.

In addition, components with a positive effect on the removability of oil and fats from textiles by washing (so-called soil repellents) may also be used. This effect becomes particularly clear when a textile which has already been repeatedly washed with a detergent according to the invention containing this oil- and fat-dissolving component is soiled. Preferred oil- and fat-dissolving components include, for example, nonionic cellulose ethers, such as methyl cellulose and methyl hydroxypropyl cellulose containing 15 to 30% by weight of methoxyl groups and 1 to 15% by weight of hydroxypropoxyl groups, based on the nonionic cellulose ether, and the polymers of phthalic acid and/or terephthalic acid known from the prior art or derivatives thereof, more particularly polymers of ethylene terephthalates and/or polyethylene glycol terephthalates or anionically and/or nonionically modified derivatives thereof. Of these, the sulfonated derivatives of phthalic acid and terephthalic acid polymers are particularly preferred.

The detergents may contain derivatives of diaminostilbenedisulfonic acid or alkali metal salts thereof as optical brighteners. Suitable optical brighteners are, for example, salts of 4,4'-bis-(2-anilino-4-morpholino-1,3,5-triazinyl-6-amino)-stilbene-2,2'-disulfonic acid or compounds of similar composition which contain a diethanolamino group, a methylamino group, an anilino group or a 2-methoxyethylamino group instead of the morpholino group. Brighteners of the substituted diphenyl styryl type, for example alkali metal salts of 4,4'-bis-(2-sulfostyryl)-diphenyl, 4,4'-bis-(4-chloro-3-sulfostyryl)-diphenyl or 4-(4-chlorostyryl)-4'-(2-sulfostyryl)-diphenyl, may also be present. Mixtures of the brighteners mentioned above may also be used.

Dyes and fragrances are added to the detergents according to the invention to improve the aesthetic impression created by the products and

to provide the consumer not only with the required washing performance but also with a visually and sensorially "typical and unmistakable" product. Suitable perfume oils or fragrances include individual fragrance compounds, for example synthetic products of the ester, ether, aldehyde, ketone, alcohol and hydrocarbon type. Fragrance compounds of the ester type are, for example, benzyl acetate, phenoxyethyl isobutyrate, p-tert.butyl cyclohexyl acetate, linalyl acetate, dimethyl benzyl carbonyl acetate, phenyl ethyl acetate, linalyl benzoate, benzyl formate, ethyl methyl phenyl glycinate, allyl cyclohexyl propionate, styrallyl propionate and benzyl salicylate. The ethers include, for example, benzyl ethyl ether; the aldehydes include, for example, the linear alkanals containing 8 to 18 carbon atoms, citral, citronellal, citronellyloxyacetaldehyde, cyclamen aldehyde, hydroxycitronellal, lillal and bourgeonal; the ketones include, for example, the ionones,  $\alpha$ -isomethyl ionone and methyl cedryl ketone; the alcohols include anethol, citronellol, eugenol, geraniol, linalool, phenyl ethyl alcohol and terpineol and the hydrocarbons include, above all, the terpenes, such as limonene and pinene. However, mixtures of various fragrances which together produce an attractive fragrance note are preferably used. Perfume oils such as these may also contain natural fragrance mixtures obtainable from vegetable sources, for example pine, citrus, jasmine, patchouli, rose or ylang-ylang oil. Also suitable are clary oil, camomile oil, nettle oil, melissa oil, mint oil, cinnamon leaf oil, lime blossom oil, juniper berry oil, vetiver oil, olibanum oil, galbanum oil and labdanum oil and orange blossom oil, neroli oil, orange peel oil and sandalwood oil.

The dye content of detergents is normally below 0.01% by weight whereas fragrances can make up as much as 2% by weight of the formulation as a whole.

The fragrances may be directly incorporated in the detergents, although it can also be of advantage to apply the fragrances to carriers



which strengthen the adhesion of the perfume to the laundry and which provide the fabrics with a long-lasting fragrance through the slower release of perfume. Cyclodextrins, for example, have proved to be suitable carriers. In addition, the cyclodextrin/perfume complexes may be coated  
5 with other auxiliaries.

In order to improve their aesthetic impression, detergents may be colored with suitable dyes. Preferred dyes, which are not difficult for the expert to select, are characterized by high storage stability and stability to the other ingredients of the detergents and to light and by no pronounced  
10 substantivity towards textile fibers so as not to color them.

The foam produced in the process according to the invention and its use as a granulation aid have not hitherto been described in the prior art. Accordingly, the present invention also relates to a surfactant foam obtainable by exposing a surfactant-containing flowable component to the  
15 action of a gaseous medium, characterized in that the foam contains anionic surfactant acid(s) and has mean pore sizes below 10 mm, preferably below 5 mm and more preferably below 2 mm.

As already emphasized in the description of the process according to the invention, a surfactant foam in which the gaseous medium makes up at least 20% by volume, based on the volume of liquid to be foamed, is preferred. In one particularly preferred surfactant foam, the gaseous  
20 medium makes up one to three hundred times, preferably five to two hundred times and more preferably ten to one hundred times the volume of the liquid to be foamed.

25 The surfactant foam according to the invention is preferably a high-surfactant foam. Surfactant foams with surfactant contents of 50 to 99% by weight, preferably 60 to 95% by weight and more preferably 70 to 90% by weight, based on the weight of the foam, are preferred.

The present invention also relates to the use of the surfactant foams  
30 according to the invention as a granulation liquid in the production of

surfactant granules. Particulars of the quantity ratios between granulation aid (surfactant foam) and the bed of solids, the mixers to be used and the ingredients suitable for use in the bed of solids can be found in the foregoing.

- 5           Embodiments of the invention are described by reference to the following specific examples which are not to be construed as limiting.

### Examples

- 10           A surfactant-containing tower powder produced by spray drying was introduced together with soda into a 20-liter Lödige plowshare mixer. The composition of the tower powder is shown in Table 1. With the mixing tools switched on, C<sub>9-13</sub> alkyl benzenesulfonic acid (ABS acid) was then introduced into the mixer as granulation aid so that the mixture was granulated. In variants E1 and E2 of the process according to the
- 15           invention, the anionic surfactant acid was brought to five times the volume by foaming with compressed air before addition to the mixer; in the case of Comparison Examples C1 and C2, the anionic surfactant acid was introduced into the mixer in liquid form. In all four cases, the ABS acid (foam and liquid) had a temperature of 60°C. After granulation for 4 minutes, the
- 20           granules were sprayed with perfume oil. After storage for 7 days at 20°C, the perfume impression was evaluated by a perfumist. Table 2 shows the composition of the granules, the oversize fraction formed during granulation and the perfume impression after storage.

**Table 1:**

Composition of the tower powder [% by weight]

C <sub>9-13</sub> alkyl benzenesulfonic acid, Na salt	22.8
C <sub>12-18</sub> tallow alcohol + 5EO	1.3
C <sub>12-18</sub> soap	1.3
Sodium sulfate	4.0
Zeolite A	48.0
Hydroxyethane-1,1-diphosphonic acid, tetrasodium salt	1.0
Sokalan® CP5*	8.0
NaOH	0.5
Water, salts	Balance

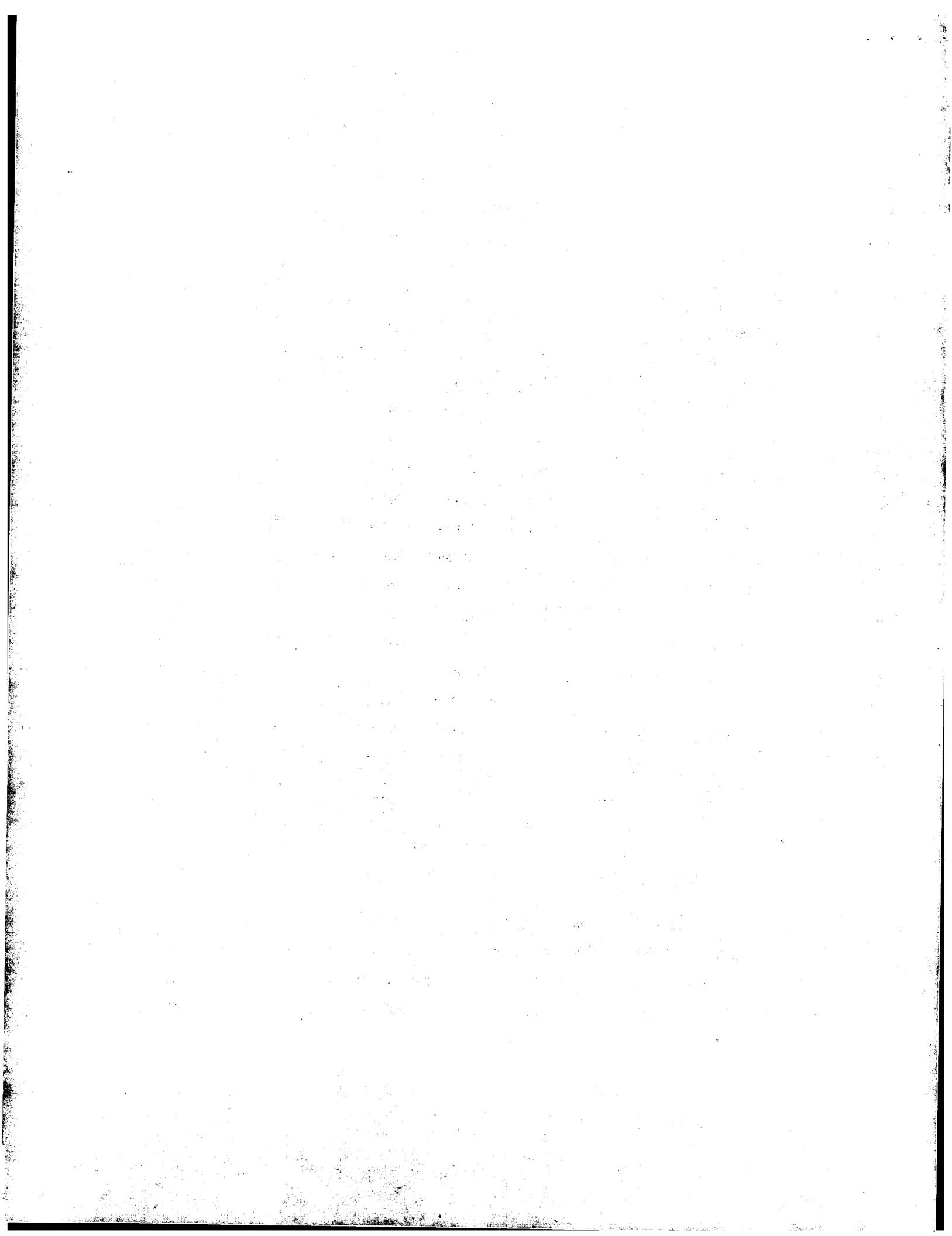
\* Sokalan® CP5 is an acrylic acid/maleic acid copolymer (BASF)

**Table 2:**

Composition of the granules [% by weight]

	E1	E2	C1	C2
Tower powder (Table 1)	65.0	72.0	65.0	72.0
Sodium carbonate	19.0	19.0	19.0	19.0
C <sub>9-13</sub> alkyl benzenesulfonic acid, foamed	15.0	8.0	-	-
C <sub>9-13</sub> alkyl benzenesulfonic acid, liquid	-	-	15.0	8.0
Perfume	1.0	1.0	1.0	1.0
Oversize fraction [% by weight > 1600 µm]	7.0	2.0	15.0	6.0
Change in perfume	No	No	Yes	Yes

Table 2 shows that, on the one hand, the percentage of coarse particles is reduced by the process according to the invention and that, on the other hand, the formation of acidic clusters and the resulting adverse effect on the perfume impression are avoided through the more uniform distribution of the acid.



**CLAIMS**

1. A process for the production of surfactant granules comprising:
  - a) foaming a surfactant-containing flowable component comprising an anionic surfactant acid, by the action of a gaseous medium to form a surfactant-containing foam; and
  - b) combining said surfactant-containing foam with a bed of solids in a mixer to form surfactant granules.
2. The process of claim 1 wherein said surfactant-containing flowable component comprises 20 to 100 percent by weight of one or more anionic surfactant acids.
3. The process of claim 2 wherein said surfactant-containing flowable component comprises 50 to 95 percent by weight of one or more anionic surfactant acids.
4. The process of claim 3 wherein said surfactant-containing flowable component comprises 60 to 90 percent by weight of one or more anionic surfactant acids.
5. The process of claim 1 wherein said surfactant-containing flowable component comprises 20 to 99 percent by weight of alkyl benzenesulfonic acids.
6. The process of claim 5 wherein said surfactant-containing flowable component comprises 30 to 95 percent by weight of alkyl benzenesulfonic acids.

7. The process of claim 6 wherein said surfactant-containing flowable component comprises 40 to 90 percent by weight of alkyl benzenesulfonic acids.
- 5 8. The process of claim 1 wherein said surfactant-containing flowable component further comprises from 1 to 30 percent by weight of fatty acids, soaps, or mixtures thereof.
9. The process of claim 8 wherein said surfactant-containing flowable component comprises from 2 to 25 percent by weight of fatty acids, soaps, or mixtures thereof.
- 10 10. The process of claim 9 wherein said surfactant-containing flowable component comprises from 5 to 20 percent by weight of fatty acids, soaps, or mixtures thereof.
- 15 11. The process of claim 1 wherein said surfactant-containing flowable component further comprises 1 to 50 percent by weight of at least one nonionic surfactant.
- 20 12. The process of claim 11 wherein said surfactant-containing flowable component further comprises 2 to 40 percent by weight of at least one nonionic surfactant.
- 25 13. The process of claim 12 wherein said surfactant-containing flowable component further comprises 5 to 30 percent by weight of at least one nonionic surfactant.
- 30 14. The process of claim 1 wherein said surfactant-containing flowable component comprises alkoxylated, nonionic surfactants.

15. The process of claim 14 wherein said surfactant-containing flowable component comprises the reaction products of C<sub>8-22</sub> fatty alcohols, with 1 to 30 moles of ethylene oxide.
- 5
16. The process of claim 15 wherein said surfactant-containing flowable component comprises the reaction products of C<sub>12-20</sub> fatty alcohols, with 2 to 20 moles of ethylene oxide.
- 10
17. The process of claim 16 wherein said surfactant-containing flowable component comprises the reaction products of C<sub>14-18</sub> fatty alcohols, with 5 to 10 moles of ethylene oxide.
- 15
18. The process of claim 1 wherein said surfactant-containing flowable component comprises less than 20 percent by weight of water.
19. The process of claim 18 wherein said surfactant-containing flowable component comprises less than 15 percent by weight of water.
- 20
20. The process of claim 19 wherein said surfactant-containing flowable component comprises less than 10 percent by weight of water.
21. The process of claim 1 wherein the quantity of said gaseous medium is one to three hundred times the volume of the surfactant-containing flowable component.
- 25
22. The process of claim 21 wherein the quantity of said gaseous medium is five to two hundred times the volume of the surfactant-containing flowable component.

23. The process of claim 22 wherein the quantity of said gaseous medium is ten to one hundred times the volume of the surfactant-containing flowable component.

5 24. The process of claim 17 wherein the gaseous medium comprises air

25. The process of claim 17 wherein said surfactant-containing flowable component to be foamed has a temperature before foaming of from 20 to 120°C.

10

26. The process of claim 25 wherein said surfactant-containing flowable component to be foamed has a temperature before foaming of from 30 to 90°C.

15 27. The process of claim 26 wherein said surfactant-containing flowable component to be foamed has a temperature before foaming of from 50 to 75°C.

20 28. The process of claim 1 wherein said surfactant-containing foam has a temperature below 115°C.

29. The process of claim 28 wherein said surfactant-containing foam has a temperature of from 20 to 80°C.

25 30. The process of claim 29 wherein said surfactant-containing foam has a temperature of from 30 to 70°C.

31. The process of claim 1 wherein said surfactant-containing foam has a density below 0.80 g/cm<sup>3</sup>.

30



32. The process of claim 31 wherein said surfactant-containing foam has a density of from 0.10 to 0.60 g/cm<sup>3</sup>.
33. The process of claim 32 wherein said surfactant-containing foam  
5 has a density of from 0.30 to 0.55 g/cm<sup>3</sup>.
34. The process of claim 1 wherein said surfactant-containing foam has a mean pore size below 10 mm.
- 10 35. The process of claim 34 wherein said surfactant-containing foam has a mean pore size below 5 mm.
36. The process of claim 35 wherein said surfactant-containing foam has a mean pore size below 2 mm.  
15
37. The process of claim 1 wherein the bed of solids introduced into the mixer comprises one or more builders.
38. The process of claim 37 wherein said builder comprises alkali metal  
20 carbonates, sulfates, silicates, zeolites, polymers, and mixtures thereof.
39. The process of claim 1 wherein said bed of solids comprises one or more alkali metal carbonates, hydrogen carbonates, or mixtures thereof in an effective quantity to neutralize the quantity of acid introduced through  
25 the foam.
40. The process of claim 39 wherein said bed of solids comprises sodium carbonate.

41. The process of claim 1 wherein said bed of solids comprises 10 to 80 percent by weight of spray-dried basic powders.
42. The process of claim 41 wherein said bed of solids comprises 15 to 70 percent by weight of spray-dried basic powders.
43. The process of claim 42 wherein said bed of solids comprises 20 to 60 percent by weight of spray-dried basic powders.
44. The process of claim 43 wherein the weight ratio of surfactant-containing foam to solids is from 1:30 to 2:1.
45. The process of claim 44 wherein the weight ratio of surfactant-containing foam to solids is from 1:100 to 9:1.
46. The process of claim 45 wherein the weight ratio of surfactant-containing foam to solids is from 1:20 to 1:1.
47. The process of claim 1 wherein said surfactant granules comprise greater than 10 percent by weight of surfactant, and have a bulk density of greater than 600 g/l.
48. The process of claim 47 wherein said surfactant granules comprise greater than 15 percent by weight of surfactant, and have a bulk density of greater than 700 g/l.
49. The process of claim 48 wherein said surfactant granules comprise greater than 20 percent by weight of surfactant, and have a bulk density of greater than 800 g/l.

50. The process of claim 1 wherein said surfactant granules have residual free water contents of from 2 to 15 percent by weight.

51. The process of claim 50 wherein said surfactant granules have residual free water contents of from 4 to 10 percent by weight.

52. A surfactant foam composition comprising an anionic surfactant acid, wherein said foam has a mean pore size below 10 mm.

53. The surfactant foam of claim 52 wherein said foam has a mean pore size below 5 mm.

54. The surfactant foam of claim 53 wherein said foam has a mean pore size below 2 mm.

55. The surfactant foam of claim 52 comprising at least 20 percent by volume of a gaseous medium.

56. The surfactant foam of claim 52 comprising 50 to 99 percent by weight of said anionic surfactant.

57. The surfactant foam of claim 56 comprising 60 to 95 percent by weight of said anionic surfactant.

58. The surfactant foam of claim 57 comprising 70 to 90 percent by weight of said anionic surfactant.

**Abstract**

The invention relates to a new granulation process in which a surfactant foam obtained by foaming a flowable component containing anionic surfactant acid with a gaseous medium is used as a granulation aid. The surfactant foam preferably has mean pore sizes below 10 mm, preferably below 5 mm and more preferably below 2 mm.